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(21) International Application Number: PCT/US96/02564 (22) International Filing Date: 11 March 1996 (11.03.96) (30) Priority Data: 08/431,003 28 April 1995 (28.04.95) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventor: BRANT, Patrick; 103 Harborcrest, Seabrook, TX 77586 (US). (74) Agents: SCHMIDT, C., Paige et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: POLYMERIZATION CATALYST SYSTEMS, THEIR PRODUCTION AND USE (57) Abstract This invention is generally directed toward a supported catalyst system useful for polymerizing olefins. The method for supporting the catalyst of the invention includes coating the supported catalyst with an inert hydrocarbon component. This provides for a supported metallocene catalyst which when utilized in a polymerization process substantially reduces reactor fouling and sheeting in a gas or slurry polymerization process.		

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POLYMERIZATION CATALYST SYSTEMS, THEIR PRODUCTION AND USE

FIELD OF THE INVENTION

5 This invention relates to catalysts, catalyst systems and to methods for their production and use in olefin polymerization. The invention particularly relates to process for preparing a supported organometallic compound for use in gas phase or slurry polymerization processes with improved reactor operability.

BACKGROUND OF THE INVENTION

10 It is widely known that olefin polymerization processes utilizing bulky ligand transition metal catalysts, otherwise known as metallocene catalysts, have been used to produce a diverse array of new polymers for use in a wide variety of applications and products. It is well known in the art that these metallocene
15 catalysts and catalyst systems are quite soluble in many liquids, particularly those diluents or reactive components used in typical polymerization processes. In addition, metallocene catalysts can also be affected chemically and physically by various components typically used in a commercial polymerization process. Metallocene catalyst components and catalyst system components have a tendency
20 toward fouling and/or sheeting in a gas phase and slurry polymerization processes. In a continuous gas phase process, in particular, fouling on the walls of the reactor, can result in many problems including poor heat transfer in the polymerization process. Polymer particles that adhere to the walls of the reactor continue to polymerize and often fuse together and form chunks, which can be detrimental to a
25 continuous process, particularly a fluidized bed process. In a continuous slurry process fouling on the walls of the reactor, which act as the heat transfer surface, can result in many problems including poor heat transfer. In addition these catalysts often provide polymer products that are low in bulk density and therefore are difficult to handle and transfer.

30 As a result of the reactor operability issues associated with using metallocene catalysts and catalyst systems various techniques for supporting or producing a metallocene catalyst system with reduced tendencies for fouling have been developed. For example, U.S. Patent No. 5,283,278 is directed towards the prepolymerization of a metallocene catalyst. While this possible solution might
35 reduce fouling or sheeting somewhat, it is expensive to employ and may not reduce

both fouling and sheeting to a level sufficient for the successful operation of a continuous process, particularly a commercial or large-scale process.

Thus, it would be highly advantageous to have an improved polymerization catalyst that in a polymerization process would significantly enhance reactor operability.

SUMMARY OF THE INVENTION

This invention is generally directed towards a new polymerization catalyst system, to methods for its manufacture and to its use in a polymerization process.

In one embodiment a method is provided to produce a supported bulky ligand transition metal catalyst system by contacting a carrier with a metallocene catalyst component and an inert hydrocarbon component.

In another embodiment of the invention a catalyst system comprising an activated metallocene catalyst on a carrier, the supported catalyst further comprising a coating of an inert hydrocarbon component.

In another embodiment of the invention, there is provided a process for producing polyolefins by contacting olefin monomer, optionally with at least one comonomer in the presence of the catalyst system described above.

In yet another embodiment there is provided a catalyst system produced by the improved method.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

This invention is generally directed toward a supported catalyst system useful for polymerizing olefins. The method for forming the catalyst system of the invention results in a polymerization catalyst with improved reactor operability.

The catalyst system of the invention not only reduces fouling and sheeting in a gas phase or slurry polymerization process but the catalyst system has better flow properties important to feeding the catalyst into the reactor. While not wishing to be bound by theory, it is believed that the inert hydrocarbon component acts as a coating for the catalyst of the invention. Additionally, it is believed that the coating provides for a catalyst system having an induction period before polymerization begins. Again, while not wishing to bound by theory, it is believed that because the catalysts of the invention are very active, the slight delay in polymerization attributable to the coating prevents the catalyst from fracturing immediately upon contact with monomer when injected into a reactor. Fracturing can result in the

production of fines which can lead to the reactor operability problems discussed above. In fact, this is contrary to the disclosure in U.S. Patent No. 5,026,797 that states that an induction period at the initiation of polymerization in a gas phase process should be avoided as far as possible. It has been demonstrated that an
 5 induction period does have several significant advantages. For example, the inert hydrocarbon component or coating in the method of the invention protects the catalyst from direct or substantial contact with typically used scavenging components used to remove impurities and other impurities introduced, present or formed during polymerization. These scavengers can interact with the components
 10 of the catalyst system to decrease catalyst activity and reactor operability.

Making the catalyst of the invention as described above results in a simple, commercially useful and cost effective supported catalyst system with a reduced tendency for sheeting or fouling in a polymerization reactor without a reduction in ultimate catalytic activity.

15 The catalyst system of the invention is useful in any polymerization process, solution, slurry, high pressure, however, a gas phase process is preferred. The tendency toward fouling and sheeting is greatly increased in a gas phase operation where a liquid is purposefully introduced into the reactor to increase cooling capacity. This type of gas phase process is known in the industry as a condensed
 20 mode polymerization process and is described in U.S. Patent Nos. 4,543,399, 4,588,790, 5,342,749, and 5,405,922. Typically the liquid utilized in such a process is an inert hydrocarbon liquid in which the metallocene and its activator is quite soluble and thus can be removed from the support material. Thus, the tendency toward fouling and sheeting in a gas phase polymerization process
 25 operating in a condensed mode when using a metallocene catalyst system is greatly increased. Also, in a slurry or bulk liquid pool polymerization process isobutane or monomer such as propylene or hexene can affect the various components of a metallocene system in the same way.

The invention provides for a polymerization catalyst that results in better
 30 reactor operability by reducing the fouling and/or sheeting tendencies particular in a continuous polymerization process.

Catalyst Components and Catalyst Systems

Preferred catalysts of the invention, for example, are typically those bulky ligand transition metal complexes derivable from the formula:



where L is a bulky ligand bonded to M, p is the anionic charge of L and m is the number of L ligands and m is 1, 2 or 3; A is a ligand bonded to M and capable of inserting an olefin between the M-A bond, q is the anionic charge of A and n is the number of A ligands and n is 1, 2, 3 or 4, M is a metal, preferably a transition metal, and $(p \times m) + (q \times n) + k$ corresponds to the formal oxidation state of the metal center, where k is the charge on the cation and k is 1, 2, 3 or 4, and B' is a chemically stable, non-nucleophilic anionic complex, preferably having a molecular diameter of 4 Å or greater and j is the anionic charge on B', h is the number of cations of charge k, and i the number of anions of charge j such that $h \times k = j \times i$.

Any two L and/or A ligands may be bridged to each other. The catalyst compound may be full-sandwich compounds having two or more ligands L, which may be cyclopentadienyl ligands or substituted cyclopentadienyl ligands, or half-sandwich compounds having one ligand L, which is a cyclopentadienyl ligand or heteroatom substituted cyclopentadienyl ligand or hydrocarbyl substituted cyclopentadienyl ligand such as an indenyl ligand, a benzoindenyl ligand or a fluorenyl ligand and the like or any other ligand capable of η -5 bonding to a transition metal atom. One or more of these bulky ligands is π -bonded to the transition metal atom. Each L can be substituted with a combination of substituents, which can be the same or different. Non-limiting examples of substituents include hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical or combination thereof having from 1 to 30 carbon atoms or silyl containing radicals. The substituent can also be substituted with hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical having from 1 to 30 carbon atoms. L may also be other types of bulky ligands including but not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. The metal atom may be a Group 4, 5 or 6 transition metal or a metal from the lanthanide and actinide series, preferably the transition metal is of Group 4. Other ligands may be bonded to the transition metal, such as a leaving group, such as but not limited to weak bases such as amines, phosphines, ether and the like. In addition to the transition metal, these ligands may be optionally bonded to A or L. Non-limiting examples of catalyst components and catalyst systems are discussed in for example, U.S. Patent Nos. 4,530,914, 4,871,705, 4,937,299, 5,124,418, 5,017,714, 5,120,867, 5,272,264, 5,278,119, 5,304,614, 5,324,800, 5,347,025, 5,350,723, 5,391,790 and 5,391,789 all of which are herein fully incorporated by reference. Also, the disclosures of EP-A-0 591 756, EP-A-0 520 732, EP-A-0 420 436, WO

91/04257 WO 92/00333, WO 93/08221, WO 93/08199 and WO 94/01471 are all fully incorporated herein by reference.

In one embodiment, the activated catalyst of the invention is formed from a catalyst compound represented by the general formula:

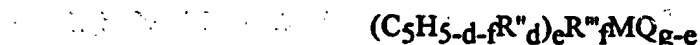


where L, M, A, and p, m, q and n are as defined above and E is an anionic leaving group such as but not limited to hydrocarbyl, hydrogen, halide or any other anionic ligands; r is the anionic charge of E and o is the number of E ligands and o is 1, 2, 3 or 4 such that $(p \times m) + (q \times n) + (r \times o)$ is equal to the formal oxidation state of the metal center, and an aluminum alkyl, alumoxane, modified alumoxane or any other oxy-containing organometallic compound or non-coordinating ionic activators, or a combination thereof.

Further, the catalyst component of the invention includes monocyclopentadienyl heteroatom containing compounds. This heteroatom is activated by either an alumoxane, modified alumoxane, a non-coordinating ionic activator, a Lewis acid or a combination thereof to form an active polymerization catalyst system. These types of catalyst systems are described in, for example, PCT International Publication WO 92/00333, WO 94/07928, and WO 91/04257, WO 94/03506, U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440 and 5,264,405 and EP-A-0 420 436, all of which are fully incorporated herein by reference. Additionally it is within the scope of this invention that the metallocene catalysts and catalyst systems may be those described in U.S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031 and 5,304,614, PCT publications WO 93/08221, WO 93/08199 and WO 95/07140 and EP-A-0 578 838, EP-A-0 638 595 all of which are herein incorporated by reference.

The preferred transition metal component of the catalyst of the invention is a Group 4 metal, particularly, titanium, zirconium and hafnium. The transition metal may be in any formal oxidation state, preferably +2, +3 or +4 or a mixture thereof, preferably +4.

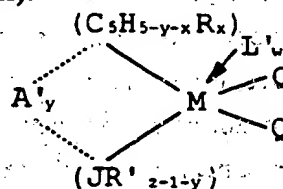
In another embodiment the catalyst component is represented by one of the formula (I):



wherein M is a Group 4, 5, 6 transition metal, at least one $(C_5H_5-d-R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to M, each R'' , which can be the same or different is hydrogen or a substituted or unsubstituted

- hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R'' is one or more or a combination of carbon, germanium, silicon, phosphorous or nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to M; each Q which can be the same or different is a hydride, substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides or any other univalent anionic ligand or combination thereof; two Q can be an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anion chelating ligand having from 1 to 30 carbon atoms, where g is an integer corresponding to the formal oxidation state of M, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3.

In another preferred embodiment of this invention the catalyst component is represented by the formula (II):



- wherein M is Ti, Zr or Hf; $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from 0 to 5 substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group 14 of the Periodic Table of Elements, and halogen radicals or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4 - C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

- (JR'^{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, y is 0 or 1, and "z" is the coordination number of the element J;

each Q is, independently any univalent anionic ligand such as halogen, hydride, or substituted or unsubstituted C₁-C₃₀ hydrocarbyl, alkoxide, aryloxy, amide or phosphide; provided that two Q may be an alkylidene, a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand;

5 A' is a covalent bridging group containing a Group 15 or 14 element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

10 L' is a Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and w is a number from 0 to 3. Additionally, L' may be bonded to any of R, R' or Q.

For the purposes of this patent specification and appended claims, the terms "cocatalysts" and "activators" are used interchangeably and are defined to be any
15 compound or component which can activate a metallocene compound as defined above, for example, a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compound that can convert a neutral metallocene catalyst component to a metallocene cation. It is within the scope of this invention to use
20 alumoxane as an activator, and/or to also use preferably bulky, compatible ionizing activators, neutral or ionic, such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl) boron or a tris(perfluorophenyl) boron metalloid precursor which ionize the neutral metallocene compound and stabilize its resulting metallocene cation.

There are a variety of methods for preparing alumoxane and modified
25 alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,278,119, 5,391,793, 5,391,529 and EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO 94/10180, all of which are fully incorporated herein
30 by reference.

Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-A-0 426 637, EP-A-500 944,
35 EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,387,568 and 5,384,299 and U.S. Patent

Application Serial No. 08/285,380, filed August 3, 1994 and are all herein fully incorporated by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, WO 94/07928, U.S. Application Serial No. 08/155,313 filed
5 November 19, 1993 and U.S. Patent No. 5,153,157 all of which are herein fully incorporated by reference.

In an embodiment of the invention two or more metallocenes as described above can be combined to form a catalyst system, see for example, those mixed catalysts described in U.S. Patent No. 5,281,679 and U.S. Application Serial No.
10 138,818 filed October 14, 1993 both of which are fully incorporated herein by reference. In another embodiment of the catalyst system of the invention combinations of one or more of catalyst components of general formula (I) and/or (II) are contemplated. In one embodiment, metallocene catalyst components can be combined to form blend compositions as described in PCT publication WO
15 90/03414 published April 5, 1990, fully incorporated herein by reference. In yet another embodiment mixed metallocenes as described in U.S. Patent Nos. 4,937,299 and 4,935,474, both are herein fully incorporated herein by reference, can be used to produce polymers having a broad molecular weight distribution and/or a multimodal molecular weight distribution.

20 In another embodiment of the invention at least one metallocene catalyst can be combined with a non-metallocene or traditional Ziegler-Natta catalyst or catalyst system, non-limiting examples are described in U.S. Patent Nos. 4,701,432, 5,124,418, 5,077,255, 5,183,867, 5,391,660 and 5,395,810 all of which are incorporated herein by reference.

25 For purposes of this patent specification the terms "carrier" or "support" are interchangeable and can be any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides, for example magnesium chloride, and resinous support materials such as polystyrene or polystyrene divinyl benzene polyolefins or polymeric compounds or any other
30 organic or inorganic support material and the like, or mixtures thereof.

The preferred support materials are inorganic oxide materials, which include those of Groups 2, 3, 4, 5, 13 or 14 metal oxides. In a preferred embodiment, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or
35 in combination with the silica, alumina or silica-alumina and magnesia, titania, zirconia, and the like.

It is preferred that the carrier of the catalyst of this invention has a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 10 to about 500 μ m. More preferably, the surface area is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 20 to about 200 μ m. Most preferably the surface area range is from about 100 to about 400 m²/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 20 to about 100 μ m. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 350 Å.

For the purposes of this patent specification and appended claims the term "inert hydrocarbon component" is any organic material that is (1) essentially unreactive toward both the individual catalyst components and the active catalyst components and the active catalyst under conditions of catalyst manufacture, handling and use during polymerization; (2) has a composition of greater than 85 weight percent hydrogen and carbon.

In one embodiment the inert hydrocarbon component has a weight average molecular weight in the range of from about 200 to about 20,000, preferably from about 500 to about 15,000, more preferably from about 500 to about 10,000, even more preferably from about 500 to about 5000.

In another embodiment, the inert hydrocarbon component is soluble at ambient or elevated temperatures which can be in the range of from 70°C to about 80°C in an aromatic hydrocarbon solvent up to at least 5 percent or greater. The hydrocarbon solvent can be for example toluene which for the purposes of this patent specification and appended claims is used.

In another embodiment the inert hydrocarbon component is a low molecular weight partially crystalline polyolefin one having a detectable melting point such a homopolymer of ethylene or propylene, or an ethylene or propylene copolymer with at least one other monomer having up to 20 carbon atoms.

In yet another embodiment the inert hydrocarbon component is a low molecular weight polymer of styrene or p-methylstyrene or other substituted styrenes or copolymers thereof including copolymers with at least one other comonomer having up to 20 carbon atoms.

In another embodiment the inert hydrocarbon component is a copolymer of one or more of the following cyclic olefins such as cyclopentadiene or combination

of cyclic olefins such as cyclopentadiene and norbornene or a combination of cyclic olefins with linear olefins, dienes, or polyenes including aromatic olefins. The copolymer comprised of these olefins is preferably hydrogenated to substantially reduce or eliminate the number of reactive double bonds.

5 In a preferred embodiment it is preferable to use an inert hydrocarbon component having a glass transition temperature (T_g) determined by Differential Scanning Calorimetry (DSC) in the range of from about 30°C to about 90°C, preferably in the range of from about 35°C to about 85°C, more preferably from about 40°C to about 80°C.

10 In another embodiment, the inert hydrocarbon component has a melting point in the range of from about 150°C to no melting point (100% amorphous material), preferably in the range of from about 140°C to about 50°C, more preferably from about 120°C to about 60°C and most preferably less than 110°C to about 60°C.

15 In an embodiment, the inert hydrocarbon component has a molecular weight distribution less than 2, preferably less than 1.8 and most preferably less than 1.5.

It is within the scope of the invention, in another embodiment, that the inert hydrocarbon component is a hydrogenated naturally occurring substance such as hydrocarbon resins, for example polyterpenes such as Zanarez, available from
20 Arizona Chemical Company, Panama City, Florida. It is also within the scope of the invention that the inert hydrocarbon can be synthetic hydrocarbon waxes, such as Escomer H series waxes, available from Exxon Chemical Company, Houston, Texas.

25 In a preferred embodiment where the activator is an ionizing component, the inert hydrocarbon component has a molecular weight in the range of about 200 to 2500, more preferably in the range of 500 to about 1500 and most preferably in the range of about 500 to about 1000. The inert hydrocarbon component typically has a peak melting point of between about 40°C and about 120°C.

30 Methods of Producing the Catalyst System of the Invention

The catalyst system of the invention can be made in a variety of different ways. Examples of supporting the catalyst system used in the invention are described in U.S. Patent Nos. 4,937,217, 4,912,075, 4,935,397, 4,937,301, 4,914,253, 5,008,228, 5,086,025, 5,147,949, 4,808,561, 4,897,455, 4,701,432,
35 5,238,892, 5,240,894, 5,332,706, and U.S. Patent Application Serial Nos. 138,818, filed October 14, 1993, 170,108, filed December 20, 1993, 182,244, filed January

14, 1994, 233,668, filed April 26, 1994, 265,533, filed June 24, 1994, 265,532, filed June 24, 1994, 271,598, filed July 7, 1994, 287,327, filed August 8, 1994, 285,380, filed August 3, 1994 and PCT Publication WO 93/11172, all of which are herein incorporated by reference. This invention in one embodiment relates to the
5 addition of an inert hydrocarbon component to any one of the methods for preparing a catalyst described in these patents and patent applications at any point during their preparation. The inert hydrocarbon component is preferably added as the last component in the method of the invention.

10 In one embodiment, at least one metallocene catalyst component, at least one activator, at least one carrier and at least one inert hydrocarbon component are combined in any order to form the supported catalyst system of the invention.

15 In one embodiment of the method of the invention a metallocene catalyst component and an inert hydrocarbon component is combined with a porous carrier containing adsorbed or absorbed water that when contacted with an organoaluminum compound forms an activator, for example the preferred organoaluminum compound being trimethylaluminum and the resulting activator being alumoxane.

20 In another embodiment of the method of the invention, a support material, a metallocene catalyst component and an activator are combined a supported metallocene catalyst precursor that is then coated with an inert hydrocarbon component. The hydrocarbon component could be added directly to the precursor in a slurry state or to the precursor in a dried state or the hydrocarbon component can be spray dried onto the precursor.

25 In one embodiment of the invention, the metallocene catalyst component and the activator can be combined to form a solution, which is then added to the carrier, followed by the addition of the inert hydrocarbon component. In another embodiment, once the solution including the metallocene component and the activator is added to the carrier or vice-versa, the latter being preferred, then the resulting mixture, typically a slurry, is dried or dried and washed at least once and
30 then dried again, and then the inert hydrocarbon component is added. In another embodiment the inert hydrocarbon component is added to the solution directly as a solid or slurried in a liquid, preferably one in which the catalyst components and the activator are insoluble. In another embodiment, the inert hydrocarbon component is added after the solution containing the activator and metallocene
35 catalyst component have been contacted with the carrier and the resulting mixture has been dried and/or dried and washed.

In another embodiment the metallocene catalyst component, the activator and the inert hydrocarbon component are added in a liquid to the carrier, preferably a liquid in which all the components are soluble, except the carrier.

5 In another embodiment the metallocene catalyst component, the activator, optionally the carrier can be added with a inert hydrocarbon component, optionally in a liquid into the reactor as a slurried mixture.

10 In one embodiment of the process of the invention, the catalyst system of the invention is prepolymerized prior to the main polymerization. For details on prepolymerization see U.S. Patent Nos. 4,923,833, 5,283,278 and 4,921,825 and EP-B-0 279 863 all of which are herein fully incorporated by reference.

15 In another embodiment of the invention, the supported catalyst system of the invention includes an antistatic agent or surface modifier, for example, those described in U.S. Patent No. 5,283,278 and U.S. Patent Application Serial No. 08/322,675, filed October 13, 1994, which are fully incorporated herein by reference. Non-limiting examples of antistatic agents and surface modifiers include, alcohol, thiol, silanol, diol, ester, ketone, aldehyde, acid, amine, and ether compounds. Tertiary amines, ethoxylated amines, and polyether compounds are preferred. The antistatic agent can be added at any stage in the formation of the supported catalyst system of the invention, however, it is preferred that it is added
20 after the supported catalyst system of the invention is formed, in either a slurry or dried state.

The preferred method for producing the catalyst of the invention is described below and can be found in U.S. Application Serial Nos. 265,533, filed June 24, 1994 and 265,532, filed June 24, 1994, both are herein fully incorporated
25 by reference in their entirety. In a preferred embodiment, the metallocene catalyst component is typically slurried in a liquid to form a metallocene solution and a separate solution is formed containing an activator and a liquid. The liquid can be any compatible solvent or other liquid capable of forming a solution or the like with at least one metallocene catalyst component and/or at least one activator. In the preferred embodiment the liquid is a cyclic aliphatic or aromatic hydrocarbon, most preferably toluene. The metallocene and activator solutions are mixed together and added to a porous support or the porous support is added to the solutions such that the total volume of the metallocene solution and the activator solution or the metallocene and activator solution is less than four times the pore
30 volume of the porous support, more preferably less than three times, even more preferably less than two times, and still more preferably in the 1.1 times to 2.7
35

times range and most preferably in the 1.2 to 2.5 times range. In another embodiment, a surface modifier is added to the catalyst preparation.

5 The procedure for measuring the total pore volume of a porous support is well known in the art. Details of one of these procedures is discussed in Volume 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total Porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, *Analytical Chemistry* 332-334 (March, 1956).

10 The mole ratio of the metal of the activator component to the transition metal of the metallocene component is in the range of ratios between 0.3:1 to 1000:1, preferably 20:1 to 800:1, and most preferably 50:1 to 500:1. Where the activator is an aluminum free ionizing activator such as those based on the anion tetrakis(pentafluorophenyl)boron as previously described, the mole ratio of the
15 metal of the activator component to the transition metal component is preferably in the range of ratios between 0.3:1 to 3:1.

The inert hydrocarbon component can be added at any stage in the preceding method of making the catalyst of the invention. Preferably, the inert hydrocarbon component is added as a solid to the solution of the metallocene
20 component and the activator component or is added after the solution is added to the porous support or is added after the mixture of the solution and the porous support is dried. In a preferred method of this embodiment, the inert hydrocarbon component in a liquid is added to the mixture of the porous support and the metallocene catalyst component and activator.

25 In any of the methods for producing the catalyst system of the invention described above, the weight percent of the inert hydrocarbon component based on the total weight of the catalyst system should typically be in the range of 0.05 to about 15 weight percent, more preferably about 0.10 to about 10 weight percent, even more preferably from about 0.15 to about 8 weight percent and most
30 preferably 0.25 to 7 weight percent.

Polymerization Process

The catalyst system of this invention is suited for the polymerization of monomers, optionally with at least one comonomer in any polymerization or prepolymerization process, gas, slurry or solution phase or a high pressure
35 autoclave process. In the preferred embodiment a gas phase or slurry phase process is utilized.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. The recycle stream usually contains one or more monomers continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. This heat is removed in another part of the process by a cooling system external to the reactor. The recycle stream is withdrawn from the fluidized bed, cooled, and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and new or fresh monomer and catalyst is added to replace the polymerized monomer and consumed catalyst. See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,382,638 and 5,352,749, 5,405,922, U.S. Application Serial No. 08/306,055 filed September 14, 1994 and U.S. Application Serial No. 08/317,136, filed October 3, 1994 and PCT patent application WO 94/28032 published December 8, 1994 all of which are fully incorporated herein by reference.

In one embodiment, the invention is directed toward a polymerization process involving the polymerization of one or more of the monomer(s) including ethylene alone or in combination with one or more linear or branched monomer(s) having from 3 to 20 carbon atoms, preferably 3 to 12 carbon atoms. The process is particularly well suited to the copolymerization reactions involving the polymerization of ethylene in combination with one or more of the monomers, for example alpha-olefin monomers of propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1, styrene and cyclic and polycyclic olefins such as cyclopentene, norbornene and cyclohexene or a combination thereof. Other monomers for use with ethylene can include polar vinyl monomers, diolefins such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, norbornene, norbornadiene, and other unsaturated monomers including acetylene, 1-alkynes and aldehyde monomers. Higher alpha-olefins and polyenes or macromers can be used also. Preferably the comonomer is an alpha-olefin having from 3 to 15 carbon atoms, preferably 4 to 12 carbon atoms and most preferably 4 to 10 carbon atoms.

In another embodiment ethylene is polymerized with at least two different comonomers to form a terpolymer and the like, the preferred comonomers are a combination of alpha-olefin monomers having 3 to 10 carbon atoms, more preferably 3 to 8 carbon atoms, optionally with at least one diene monomer. The preferred terpolymers include the combinations such as ethylene/butene-1/hexene-

1, ethylene/propylene/butene-1, ethylene/propylene/hexene-1, ethylene/propylene/norbornadiene, ethylene/propylene/1,4-hexadiene and the like.

In one embodiment a scavenger can be used, however, in another preferred embodiment, the process of the invention does not require a scavenger, non-limiting examples of scavenger compounds include for example, triethylaluminum (TEAL), trimethylaluminum (TMAL), tri-isobutylaluminum (TIBAL) and tri-n-hexylaluminum (TNHAL) and diethyl aluminum chloride (DEAC) and the like.

In another embodiment of the process of the invention an inert hydrocarbon component or antistatic agent as described in U.S. Patent No. 5,238,278 and U.S. Application Serial No. 08/322,675, filed October 13, 1994 can be introduced into the reactor together, separately or apart, from the catalyst system of the invention.

A slurry polymerization process generally uses pressures in the range of about 1 to about 500 atmospheres or even greater and temperatures in the range of -60°C to about 280°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, isobutylene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or isobutane is employed. A non-limiting example of a slurry process can be found in PCT Publication WO 94/21691, published September 29, 1994 which is herein fully incorporated by reference.

It is within the scope of this invention that during the process of the invention that the catalyst system of the invention has an induction period greater than about 2 minutes as measured in a slurry polymerization process. In one embodiment, the induction period (period of catalyst inactivity) is greater than 2 minutes, preferably greater than about 3 minutes and more preferably greater than 5 minutes.

30. EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

The properties of the polymer were determined by the following test methods: Melt Index is measured in accordance with ASTM D-128-Condition E. Density is measured in accordance with ASTM-D-1238.

All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect. In the Tables the abbreviations, XRF = X-ray fluorescence and, NCE = normalized catalyst efficiency. In Example 1 and Comparative Example 2, "Davison 948 silica calcined at 800°C", (available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland) represents silica support which has been calcined at 800 °C under a dry N₂ flow for 8-24 hours, so as to achieve a hydroxyl content of 0.2-0.5 mmol/g silica.

CATALYST PREPARATIONS

EXAMPLE 1

50.0 grams of silica (Davison 948, calcined at 800 °C) was slurried in 500 mL of pentane at 25 °C under nitrogen in a 1-L round bottom flask, and 50 mL of a 24.8% TEAL (triethylaluminum) solution in heptane was added slowly. Stirring was continued for 30 minutes, at which time the TEAL treated silica was isolated by filtration, and washed with three 150 mL portions of pentane, and residual solvent removed in vacuo, to yield 55.4 grams TEAL treated silica. A solution of activated catalyst was prepared by combining 2.00 g [DMAH]⁺[(pfp)₄B]⁻ and 0.973 g (1,3 BuMeCp)₂ZrMe₂ (bis(1,3-butylmethylcyclopentadienyl)zirconium dimethyl) in 10 mL toluene, and stirring until gas evolution ceased (about 15 min). This solution was pipetted into a slurry composed of 50.0 g of the aforementioned TEAL treated silica in 500 mL of toluene at 25°C under nitrogen in a 1 L round bottom flask. After stirring for 20 min, the solvent was removed in vacuo. This material was reslurried in 500 mL of pentane at 25°C under nitrogen in a 1 L round bottom flask, and to it was added 4 g polyparamethylstyrene, the inert hydrocarbon component or coating, (M_w = M_n = 2000) in 250 mL pentane. After about 20 min of stirring, the pentane was removed in vacuo, to yield 55 g of a free flowing solid supported catalyst.

COMPARATIVE EXAMPLE 2

This catalyst was prepared as per Example 1 except that the addition of polyparamethylstyrene was omitted.

EXAMPLE 3

The supported catalyst of this example was prepared from 800 lbs (364 kg) of silica (Davison 948 available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland) dehydrated at 600 °C. The catalyst was a commercial scale catalyst prepared in a mixing vessel with an agitator. An initial charge of 1156 pounds (525 kg) toluene was added to the mixer. This was followed by mixing 925 pounds (420 kg) of 30 percent by weight methyl alumoxane (MAO) in toluene (available from Albermarle Corporation, Baton Rouge, Louisiana). This was followed with 100 pounds (46 kg) of 20 percent by weight bis(1,3-methyl-n-butyl cyclopentadienyl) zirconium dichloride in toluene (20.4 pounds (9.3 kg) of contained metallocene). An additional 144 pounds (66 kg) of toluene was added to the mixer to rinse the metallocene feed cylinder and allowed to mix for 30 minutes at ambient conditions. The above mixture was added to the silica after which 54.3 pounds (25 kg) of a Kemamine AS-990 in toluene solution, surface modifier solution, containing 5.3 pounds (2.4 kg) of contained Kemamine AS-990 (available from Witco Chemical Corporation, Houston, Texas). An additional 100 pounds (46Kg) of toluene rinsed the surface modifier container and was added to the mixer. The total liquid volume was equivalent to 2.4 cc/cc pore volume of the silica. The resulting slurry was vacuum dried at 3.2 psia (22 kPa) at 175°F (79°C) to a free flowing powder. The final catalyst weight was 1093 pounds (497 kg). The catalyst had a final zirconium loading of 0.40 weight percent and an aluminum loading of 12.0 weight percent.

1.0 g of Multiwax 195 M having a number average molecular weight of 760 molecular weight distribution of 1.2 and a melting point of 87°C (available from Petrolyte Corporation, Tulsa, Oklahoma) was placed, along with 60 mL dry toluene, in a three neck 500 mL flask equipped with two stoppers and a vigreux column. This mixture was heated to 92°C with stirring until the Multiwax dissolved. Then, to the hot solution 30 g of the supported catalyst prepared above was slowly added with manual stirring. After 20 g of the supported catalyst was added, 20 mL additional toluene was added to the mixture, and then the final 10 g of supported catalyst added. The product was removed from the heat, a fritted adapter placed on the flask, and the flask evacuated overnight. The dried catalyst was screened through a 35 mesh sieve and the majority of the sieved product transferred directly to a stainless steel pressure vessel. The sieved product had good flowability.

EXAMPLE 4

Into a 600 mL beaker was placed 49.3 mL of dry toluene along with a magnetic stirring bar. To this solvent was added 2.0 g of crushed Escorez 1310LC tackifier available from Exxon Chemical Company, Houston, Texas. Once the tackifier was dissolved, 0.78 g of $(1,3\text{-BuMeCp})_2\text{ZrCl}_2$ was added and also dissolved. Then, 39.0 mL of methylalumoxane (MAO) in toluene (30% by weight MAO, available from Albemarle, Baton Rouge, Louisiana) was added. This combined solution was allowed to stand with stirring for about 15 minutes. Over a period of about 5 minutes, 30.0 g of Davison 948 silica dehydrated at 800°C (available from Davison Chemical Company, Baltimore, Maryland) was added to the solution with manual stirring. Following complete contact of silica with catalyst solution, the product was transferred to an 8 oz bottle fitted with a fritted adapter. The adapter was connected to a vacuum and the product dried in vacuo such that the residual toluene in the preparation was less than 1 wt%.

EXAMPLE 5

Inside a dry box, 16.8 mL of toluene and 0.26 g of $\text{bis}(1,3\text{-BuMeCp})\text{ZrCl}_2$ metallocene catalyst component were placed in a 250 mL three neck flask equipped with two stoppers and a vigreux column. Once the metallocene catalyst component was dissolved, 13.0 mL of 30% by weight MAO in toluene available from Albermarle, Baton Rouge, Louisiana was added to the flask to form a solution. The solution was then heated with stirring to 65°C. Then 2.0 g of Multiwax 195 M was added to the flask and the temperature raised to 80°C. The temperature was further raised to 85°C and the wax was fully dissolved. At this point 10 g of 800°C Davison 948 silica was added to the solution with magnetic stirring. A further 10 g of the silica was then added. Magnetic stirring was complemented by stirring with a spatula. At the end of the silica addition, the flask was removed from the heat and a fritted adapter placed on the flask. Then the flask was evacuated overnight inside the drybox. The dried catalyst was transferred to a glass storage vessel and sealed.

EXAMPLE 6

Inside a drybox, 49.3 mL of toluene and 2.0 g of Multiwax 195 M (as described above) were placed along with a teflon coated stir bar in a 500 mL three neck flask equipped with two stoppers and a vigreux column. This mixture was heated with stirring to 97°C to dissolve the wax. Once the wax was dissolved, the

solution was coated to 92°C and 0.78 g of bis(1,3-BuMeCp)ZrCl₂ metallocene catalyst component was added with continued stirring. This was followed by the addition of 39 mL of 30 wt% MAO (as above) in toluene. About 5 minutes after addition of the MAO, 30 g of 800°C Davison 948 silica was slowly added to the flask. The magnetic stirring was complemented by stirring with a spatula. At the end of the silica addition, the flask was removed from the heat and a fritted adapter placed on the flask. Then the flask was evacuated overnight inside the drybox. The following day, the dried product was sieved through a #35 mesh (500 micron) sieve and the sieved product transferred to a stainless steel catalyst storage and transfer cylinder.

EXAMPLE 7

This catalyst was prepared as per Example 6 except only 0.5 g of Multiwax 195 M was added.

EXAMPLE 8

Another sample of the identical catalyst prepared in Example 3 was used.

POLYMERIZATION TESTS

A sample of each supported catalyst in Example 1, Comparative Example 2 and Example 3 described above were used for ethylene/1-hexene copolymerization studies as described below. A continuous fluid bed gas-phase reactor operated at 300 psig (2069 kPa) total pressure, 145°F (63°C) reactor temperature and 0.7 ft/s (21.3 cm/s) cycle gas velocity was used for determining catalyst efficiency and response to co-monomer such as 1-hexene. A solution of TEAL (1 wt% in isopentane) was fed into the reactor as a scavenger at a rate of 1 cm³/h. A summary of the process data is included in Table 1. Polymer samples were collected and analyzed after at least three bed turnovers.

TABLE 1

PROCESS DATA	Example 1	Comparative Example 2	Example 3
H ₂ conc. (ppm)	62	62	82
C ₆ /C ₄ conc. (mol%)	0.68	0.70	0.52
C ₂ conc. (mol%)	34.7	36.0	30.4
H ₂ /C ₂ Ratio	1.8	1.7	2.7
C ₆ /C ₂ Ratio	0.020	.020	0.017
Reactor Temp °F (°C)	145 (63)	147 (64)	155
Avg. Bed weight (g)	431	434	422
Production (g/hr)	123	143	169
Productivity (g/g) - XRF	889	504	714
NCE (g/g*hr*atm) XRF	36	23	46
Total Bed Turnovers	9.6	4.6	7.2
POLYMER DATA			
MI (g/10 min)	15.22	12.83	1.78
density (g/cc)	0.9107	0.9109	0.916
bulk density (g/cc)	0.4490	0.3655	0.41

5 The catalyst of Example 1 ran well, it did not produce chips or chunks, and produced polymer of a high bulk density, indicating the absence of extensive (and premature) fracture of the supported catalyst in the early stages of polymerization.

10 The catalyst of Comparative Example 2 did not run as smoothly as it's coated analog, Example 1, and the reactor had to be shut-down due to the formation of a large polymer chunk in the reactor, leading to a loss of fluidization. The bulk density of the polymer produced was lower than that produced by catalyst of Examples 1 and 3, indicating premature fracture of supported catalyst particles.

15 A sample of each of the supported catalysts described in Examples 5, 6, 7 and 8 were used for ethylene/1-hexene batch slurry polymerizations as follows. Polymerizations were performed in 400 mL of dry hexane in a nitrogen purged 1 L Zipperclave reactor (Autoclave Engineers) equipped with an external temperature control jacket. In a glove box a charge of the supported catalyst, 100 mg, was loaded into a short length of SS tubing between two ball valves and backed by a small bomb containing 20 mL dry hexane. This device was attached to the reactor under a N₂ purge. 0.200 mL 25 wt% triethylaluminum in heptane and 45 mL of
20 dry 1-hexene were injected into the reactor and the mixture heated to 60°C under

stirring. Stirring was stopped and the supported catalyst flushed into the reactor under 75 psi (517 kPa) ethylene pressure. Stirring was immediately restarted while the reactor reached its regulated operating pressure of 75 psi (517 kPa) ethylene (plus solvent vapor pressure). After 30 minutes and 60 minutes for some of the catalysts the reactor was vented and the contents emptied into a beaker in air and filtered. The catalysts of Examples 5 and 6 were each used in a 30 minute polymerization run and a 60 minute run. The 60 minute polymerization runs using the same catalyst produced in Examples 5 and 6 are identified as Example 5A and Example 6A in Table 2.

TABLE 2

Example	Reaction Time (minutes)	Yield (g)	Induction Period (minutes)	Mw	Mn	Mz	Peak MP (°C)
5	30	4.7	~5	181	74	351	98
5A	60	18.5	~5	172	71	339	117
6	30	13.4	~7	168	73	311	97
6A	60	32.6	~7	174	75	315	99
7	30	19.7	~3	—	—	—	—
8	30	16.3	~3	—	—	—	—

While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. The catalyst of the invention can be used in a single reactor or in a series reactor or even in series where one reactor is a slurry reactor and the other being a gas phase reactor. It is contemplated that the catalyst of the invention can be mixed with a traditional Ziegler-Natta catalyst or a catalyst of the invention can be separately introduced with a traditional Ziegler-Natta catalyst or any other metallocene catalyst system with or without a inert hydrocarbon component. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

1. A method for forming a supported catalyst system, the method comprising combining a carrier, a metallocene catalyst component, an activator and a inert
5 hydrocarbon component having a weight average molecular weight in the range of from 200 to 20,000.
2. The method of claim 1 wherein the inert hydrocarbon component is present in an amount in the range of from 0.05 weight percent to less than about 10 weight
10 percent of the total weight of the supported catalyst system.
3. The method of any of the preceding claims wherein the inert hydrocarbon component has a number average molecular weight distribution less than 2.5.
- 15 4. The method of any of the preceding claims wherein the inert hydrocarbon component has a glass transition temperature (T_g) in the range of from 30°C to 90°C.
- 20 5. The method of any of the preceding claims wherein the inert hydrocarbon component is a styrene homopolymer or copolymer of styrene and at least one other comonomer having up to 20 carbon atoms.
- 25 6. The method of any of the preceding claims wherein the inert hydrocarbon component is a partially crystalline ethylene or propylene homopolymer or copolymer of ethylene or propylene with at least one comonomer having up to 20 carbon atoms.
- 30 7. The method of any of the preceding claims wherein the activator is an alumoxane.
8. The method of any of the preceding claims wherein the method further comprises the step of first drying the combination of the carrier, the metallocene catalyst component and the activator and then adding the inert hydrocarbon
35 component.

9. The method of any of the preceding claims wherein the metallocene catalyst component and the activator are combined to form a reaction product that is then added to the porous carrier.
- 5 10. A process for polymerizing olefins alone or in combination with one or more other olefins, said process comprising polymerizing in the presence of a supported catalyst system of any of the preceding claims.
- 10 11. A catalyst system produced by the method of any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/02564

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/609

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO,A,96 11960 (EXXON) 25 April 1996 see page 23; example 21 see claims 1-4	1,2,9-11
X	WO,A,94 26793 (EXXON) 24 November 1994 see page 17; example 8	1
A	EP,A,0 519 236 (BASF) 23 December 1992 see page 4, line 45 - line 50 see claims 1,5,7,8 see page 5; example 1	1
A	EP,A,0 567 952 (HOECHST) 3 November 1993 see page 15; examples 1,2	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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